LIQUID AMMONIA AS SOLVENT IN THE SILVER COULOMETER

A Thesis

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By

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LIQUID AMMONIA AS SOLVENT IN THE SILVER COULOMETER

INTRODUCTORY AND HISTORICAL.

Although Faraday's law holds true for nearly every ionized substance in solution, very few substances have been found which possess a practical value for the accurate measurement of electrical quantity. One of the simplest methods for this purpose is the decomposition of water, but even if an accurate observation of the volume of gas given off be taken, other factors would render the determination approximate only. Among these disturbing factors might be mentioned the occurence of side reactions and the dissolving of the gases by the electrolyte, both taking place only to a very small extent, but sufficient to make worthless any attempt at extreme accuracy. The deposition of copper from its solution onto a cathode presents a means for measuring electricity which is much used. Complications occur here, however, such as the formation of hydrogen, cuprous compounds or the oxide at the cathode, and the measurements obtained may be depended on only to about one tenth of one per cent.

The conditions which must be fulfilled in an ideal coulometer might be formulated as follows.

1.The deposit must be one definite substance,and nothing but that substance.

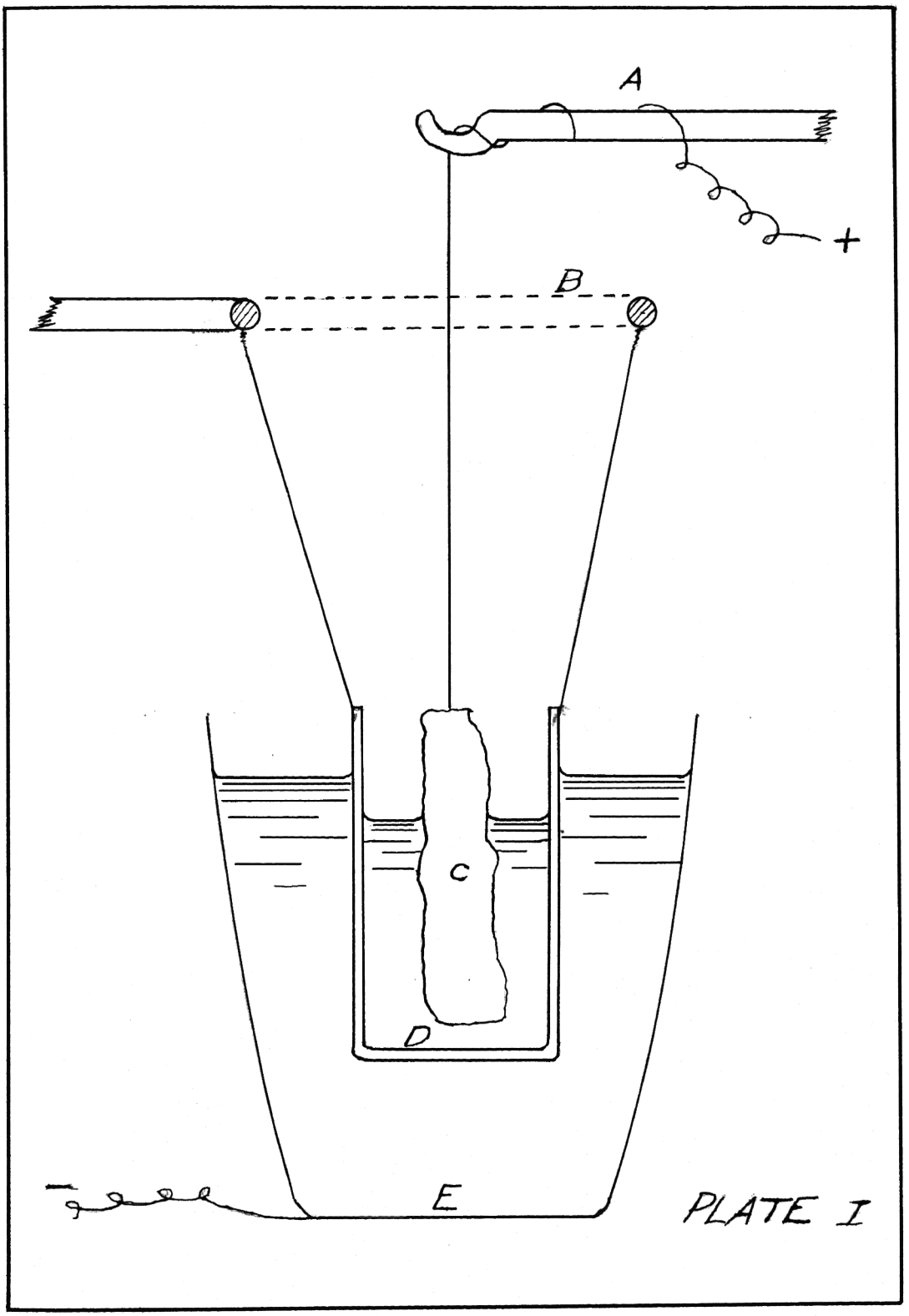
2.The deposit must all be due to the action of the current. That is,nothing must be mixed with the deposit mechanically so as to analyse as part of the electrolytic deposition.

3.The deposit must not be acted on by the electrolyte or the air.

4.The deposit must be in such a form or of such a nature that it may be conveniently weighed or analysed.

5.There must be no drift of the electrolyte from the anode to the cathode,if cations other than those desired are formed at the anode.

The instrument which fulfills these conditions to the greatest extent,so far as known,is the standard silver coulometer. A sketch of this instrument,as devised by Richards,is shown on the accompanying plate. E is a rather large platinum crucible,resting on a metallic mat,which is connected with the source of the negative current. The electrolyte,consisting of a fresh 10-20% solution of silver nitrate,is contained in this crucible. C is the anode,


A
+
B
C
D
E
PLATE I

suspended from an insulated glass support A by means of a silver strip. To prevent the diffusion of the liquid around the anode over to the cathode(because of side reactions at the anode),the silver anode is contained in a porous cell D,which should approximate 50 mm. in height, 20 mm. in diameter,and the walls of which should not exceed 1 mm. in thickness. This porous cell is suspended from the top by platinum wires to a thoroughly insulated glass ring B.In order to insure the absence of drift in the anolyte,the liquid inside the porous cell has a slightly lower level than that outside;if there is any tendency to diffusion,it will occur toward the anode instead of away from it. The entire arrangement is protected from dust by a hood.

Electrical quantity is measured by this coulometer as follows. The platinum containing dish,which also serves as cathode,is carefully cleaned,rinsed with alcohol,and dried at 160 degrees for one hour. After drying,the cathode is allowed to rest in a dessicator for two or three hours,and immediately weighed. The porous cell is boiled in dilute nitric acid,and thoroughly rinsed with distilled water. The anode receives similar treatment. The platinum crucible is nearly filled with double distilled water,

and two or three grams of the purest silver nitrate added and stirred to solution. The various parts are put in place,and by means of a dropper some of the electrolyte is transfered to the interior of the porous cell,so that the level of the solution inside is a little lower than that of the solution outside of the anode chamber. After the proper connections have been made,the coulometer is ready to measure the electricity sent through it. For accurate work, the current density must be limited to .01 ampere per sq.cm.of cathode surface. For an apparatus of the size described,the total deposit must not be more than three or four grams.

When the current has been shut off,the cathode vessel is immediately removed. The electrolyte is poured off with due care that no minute particles of silver are carried off with it. According to Richards the electrolyte should be filtered when pouring it off,preferably thru a Gooch crucible. The present research indicates,however, that errors due to the loss of silver in this manner are smaller than those caused by the difference in the weights of a Gooch crucible at different times,even when heated, dried and weighed under the same laboratory conditions. The deposit is rinsed twice with water,being careful to

observe the precaution mentioned above. More water is put in the vessel,and allowed to stay there for two or three hours,and then a final portion is poured in to remain over night. When this has been poured off,the crucible is rinsed with alcohol,dried at 160 degrees for one hour, cooled in a dessicator for a period of two or three hours and immediately weighed. The difference between the original weight of the crucible and the final weight gives the deposit,and from this,the equivalent weight of silver, and the value of the faraday in coulombs,the quantity of electricity passed through the coulometer is determined.

The only question as to the validity of the results obtained by the silver coulometer is as to whether the deposit weighed is all silver and was all deposited by the action of the current,or as to the possibility of any other substances other than silver being deposited at the cathode electrolytically. This last named possibility can not occur because no other cations are present in the electrolyte in sufficient concentration to be reduced at the cathode at the potential difference of the experiment.

The problem of the purity of the silver deposit has, however,been one fruitful of much investigation. No free

silver could be present in the cathode deposit,except that formed by the electric current,since this current is the only reducing agent present. Any impurity in the silver deposit must therefore be mechanically included, and so surrounded by free silver that it is impossible to wash it out.

Rayleigh and Sedgwick* were the first ones to suspect that the deposits in the silver coulometer were not all pure silver. The basis for their hypothesis lay in the fact that silver nitrate containing a minute amount of silver acetate as an impurity gave finer,more coherent and heavier deposits than silver nitrate of an extra grade of purity. Furthermore,on heating the crucible containing the deposit over a Bunsen burner,a noticeable loss in weight was observed,due,as they suspected,to the volatilization of certain of the impurities included in the deposit. The average loss in weight due to heating was found to be .007 per cent.

Another investigation with an entirely different line of procedure was undertaken by Richards,Collins and

* Phil.Trans.,175,111.

Heimrod.* They analysed the silver deposit by dissolving it in nitric acid,and precipitating and weighing as the bromide. The results obtained vary between wide limits,but the average deficiency in the silver analysed as compared with the original deposit was .006%. This method was too inaccurate for conclusive evidence,so further research was necessary to prove the existence of any impurities in the silver deposit.

Other attempts than the two described above have been made to solve the problem,some showing the presence of impurities,and others,equally as accurate in principle, showing the absence of any appreciable quantity of included matter.

Laird and Hulett** have finally proven beyond question of doubt that the deposit of the standard silver coulometer contains quite appreciable amounts of included substances. They reasoned that if some suitable metallic solvent could be found for silver,but which was not a solvent for the inclusions,the latter would be released as gases,and could be measured by the pressure they would exert in a containing vessel.

*Proc.Amer.Acad.,35,133.
**Trans.Amer.Electrochem.Soc.,Vol.22.

A very brief description of the apparatus used by Laird and Hulett will not be out of place here, since they have shown so conclusively the presence of impurities in silver deposits. A bulb containing tin, kept molten by means of an electric furnace, was connected to the rest of the apparatus by a tube so arranged that the silver deposit under examination could be thrown into the molten bath when so desired. The whole arrangement was perfectly air tight and was evacuated to the highest degree possible. The pressures developed by the gaseous inclusions given off when the silver dissolved in the molten tin were measured by a sensitive mercury manometer. A coil of copper oxide, heated by an electric current, served to oxidize all reducing gases which may have been given off from the molten bath. An analysis of the gases in the apparatus was now possible by means of fractional condensation. The water vapor was condensed by surrounding a small side tube with a proper freezing mixture, the carbon dioxide with liquid air, while the nitrogen remained in the apparatus uncondensed. By observations of the pressures after each condensation, the amount of each impurity in the silver deposit was very accurately determined.

The results obtained by this very ingenious method throw the first definite light on the ~~subject of the~~

subject of the inclusions in electrolytic silver. The table below shows an interesting comparison between the deposits on platinum and on gold,using as electrolyte very pure silver nitrate,and the deposit in the old Rayleigh form of coulometer,where the anode was protected by filter paper and commercial C.P. silver nitrate used.

	Platinum	Gold	Rayleigh
Per cent water per gram silver	.004	.0037	.0051
Mm.residual gas per gram silver	16	24	50

From these results the principal fact to be observed is that the amount of inclusion when C.P.silver nitrate of a commercial grade is used is about three times that when the purest silver nitrate serves as electrolyte. The results given above for the platinum were found to hold for all the trials,with a reasonable allowance for error.

Another instructive set of observations was taken with regard to the effect of the diffusion of the anolyte to the cathode. Two sets of runs were made,one where the anolyte diffused to the catholyte,and another where the reverse process took place. The results are given below in percentages.

	Water	CO_2	$AgNO_3$
Catholyte mixed with anolyte	.0046	.00065	.00104
Catholyte free from anolyte	.0042	.00042	.00053

It may be seen that the total quantity of impurity is changed by the diffusion process, proving the necessity of the porous anode cell. This difference would be increased somewhat, if the carbon dioxide were assumed to be present in the silver deposit as silver carbonate, which appears probable, according to Laird and Hulett.

The results of this investigation show that the silver deposit obtained from the purest silver nitrate solution free from traces of filter paper is heavier by at least 5 parts in 100,000 than it should be. The presence of small amounts of impurity in the silver nitrate or in the water increase the inclusions very appreciably.

LIQUID AMMONIA AS THE SOLVENT

It was with the idea of eliminating these inclusions in the silver coulometer deposit that Dr. H. P. Cady suggested the use of liquid ammonia as solvent instead of water. From the previous researches of Dr. Cady and his assistants it had been noted how much more coherent and smoother the deposits of silver from liquid ammonia solutions were than those from aqueous solutions. To determine whether the smooth, coherent deposit included more or less foreign matter than the loose crystalline silver obtained from water solutions was the purpose of the present research.

The plan to be followed in working this out was as follows. First,a standard silver coulometer and another coulometer which contained liquid ammonia instead of water were to be connected in series,and a comparison of the weights of the two respective deposits made. Second,in case the results obtained by this first method showed very little difference in weight between the deposits,a more accurate analysis was to be made of this silver by some method similar in principle to that used by Laird and Hulett,as just described.

APPARATUS

The standard silver coulometer used was that shown on Plate I. The platinum crucible rested on a mat of fine copper wires connected to the source of the negative current. The porous anode cell was approximately of the dimensions given earlier in this paper,and was supported from an insulated glass ring by platinum wires. The anode was roughly cylindrical in shape,40 mm.long and 5 mm.in diameter. The method used to make this anode was to melt pure silver in a small crucible and pour the molten metal into a charcoal mold. The charcoal had the effect of absorbing any gases given out by the cooling silver,and also possessed the advantage of not fouling the silver in any way. The anode was attached to the copper lead above by a strip of pure silver. The silver nitrate used was the purest obtainable,and the water was double distilled

conductivity water.

Various arrangements were tried in order to get a satisfactory liquid ammonia silver coulometer. To use the same form as the ordinary silver coulometer was impracticable because of the rapid evaporation of the liquid ammonia when exposed to the heat of the room. A specially constructed bomb would be needed to keep the liquid under pressure,so this would be available only as a last resort.

A platinum crucible containing the usual arrangement of porous cell,anode,and electrolyte was lowered into a tube contained in a Dewar bulb. Inside the bulb and surrounding the inner tube,liquid ammonia was poured as a refrigerant for the liquid in the coulometer. Although by this method the electrolyte lasted longer than when exposed directly to the atmosphere,the apparatus was inconvenient to handle,the run had to be short because of the small amount of electrolyte,and the apparatus was abandoned after one trial.

The problem was to get an apparatus having a comparitively large bath of electrolyte protected from exterior heat as far as possible. The cathode did not need to be the containing vessel,as there was no danger of mechanical loss of the deposit. Neither did the cathode have to

be platinum,since silver would serve the purpose just as well.

It was from these considerations that the arrangement shown on Plate II was devised. A is a Dewar bulb,unsilvered,so that everything inside is in sight all the time. B is the cathode;this is made of thin rolled silver,and is in the form of a cylinder,open at both ends. This cylinder is 2 cm.high and 4 cm.in diameter. It is supported in the bath by a thin strip of pure silver,welded to the cathode and attached at the other end to a platinum ring which is sealed in the end of a glass tube. The platinum extends up into the tube where connection is made to the source of current by a mercury contact. The anode C is made in the same way as the anode for the standard coulometer was,and is suspended by a platinum wire sealed in the end of a glass tube;connection is made to the positive current by a mercury contact. D is a porous cell similar to that used in the other coulometer and suspended by two platinum wires which are made fast by means of a small stout rubber to the glass tube to which the anode is attached. E is a vessel of water arranged so that the fumes from the liquid ammonia will be absorbed instead of passing out into the room.

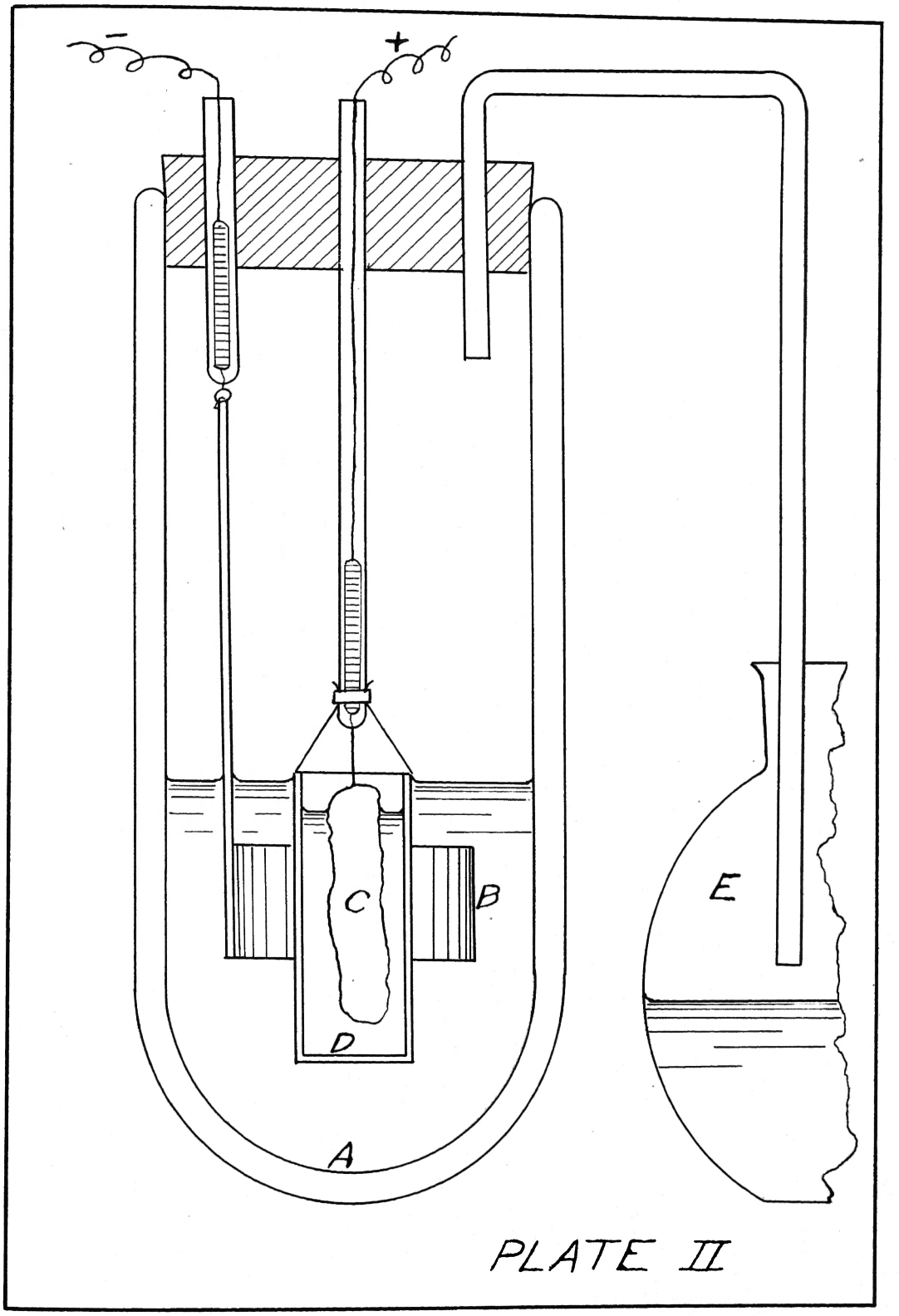


PLATE II

This final arrangement was found very satisfactory. The current could be run several hours before the bath was so low that it had to be shut off. Everything was in sight all the time. The cathode could be easily placed or removed,and the porous cell and anode could be lowered as the level of the electrolyte became lower. With this apparatus there was no necessity for pouring liquid ammonia, a disagreeable operation at the best.

The oven used to heat the deposits on the platinum crucible was gas fired and provided with a thermometer. A support of glass held the crucible while drying.

In order that the weighings should be as accurate as possible,they were all done on a balance sensitive to one hundredth of a millegram. The weights were calibrated against U.S.Bureau of Standards weights.

METHOD

The method of running the determinations was changed several times in small detail during the investigation, but that finally used and found to give the best results was as follows. The procedure for the operation of the standard silver coulometer has already been given,and this was followed in detail for all the runs.

It was found,for reasons that will be given later,that the cathode of the liquid ammonia coulometer had to be heated very hot in order to get the deposit as pure as possible. To render the conditions of drying and cooling the same before as after the run,it then became necessary to heat the silver cathode at the beginning. After the usual processes of washing with water and rinsing with absolute alcohol,the cathode with the attached supporting wire was placed in a crucible. This was put in a small melting furnace and the blast so regulated that the silver was held from 100-200 degrees below its melting point for 15-20 minutes. It was quickly removed to a dessicator,allowed to stay there for at least one hour,and weighed.

The Dewar bulb was now thoroughly cleaned and dried,and was attached to the delivery tube of a cylinder of liquid ammonia. When the bulb was about half full(60 cc.),the liquid was shut off. About three grams of finely pulverized pure silver nitrate was slowly added to the liquid in the bulb,and the mixture allowed to stand,with frequent stirring, until solution was complete.

The porous cell was boiled in nitric acid and thoroughly rinsed with distilled water. The silver anode was likewise treated with nitric acid and rinsed.

The cathode,anode and porous cell were hung from their proper places,and the stopper was placed in the mouth of the Dewar bulb,thus lowering them into the bath. The anode was lowered just so the liquid ammonia solution could run into the porous cell,and was then lifted clear of the bath. This was done so that some of the liquid ammonia could evaporate,and make the level of the liquid inside the cell somewhat lower than that outside. As has been stated before, this is always done in accurate coulometer work,for the reason that certain by-products are formed at the anode, which would interfere with a perfect deposit were they allowed to drift to the cathode. The anode was then lowered again until the top of the porous cell just projected above the level of the bath. During the run it was kept in this relative position by pushing down the tube supporting the anode every ten or fifteen minutes.

The apparatus was then ready for work,and was connected in series with the standard coulometer,a water rheostat, and an ammeter reading upto one ampere. The current for these investigations was obtained from storage batteries, so there was little fluctuation. This current was so regulated by means of the conductivity of the rheostat water that it varied very little from 100 milleamperes. For the

size of cathode used,this meant a current density of .004 ampere per sq.cm. Very little regulation of the current was required after starting,and about the only attention necessary was to see that the porous cell was always well down in the solution.

After running about three hours,the current was shut off. The cathode was carefully removed from the Dewar bulb,and allowed to warm up in the air for a minute. It was then plunged into a bath of fairly strong ammonia water,the purpose of which will be indicated later. The silver cathode soaked in this aqueous ammonia for several hours,when it was removed,washed with distilled water,rinsed with alcohol, and heated,dried and weighed under exactly the same conditions as before the run. The mode of procedure in the case of the standard coulometer has already been given. The weights of each deposit are then known,and may be compared.

RESULTS

Fifteen runs were made in all,but only nine yielded quantitative results. Two runs were spoiled when the deposit on the platinum crucible built out in fine thread like growths clear over to the anode cell,thus short circuiting the current through the electrolyte. The only explanation offered for this phenomenon is that the porous cell was soaked in

very dilute ammonia water just previous to the run,from which fact it might be deduced that it were better to have the electrolyte very slightly acid rather than very slightly alkaline. In some of the runs no effort was made for quantitative results,but merely the nature of the deposit was studied.

With the two exceptions mentioned above,no trouble was experienced with the standard coulometer. Some of the crystalline deposits obtained were rather loose,and great care had to be taken that no fine particles of silver were lost. A coulometer of this type operates with an accuracy of 5 parts in 100,000,when run according to specifications. As stated previously,the inclusions in silver deposits have been found to be at least 5 parts per 100,000,if absolutely pure silver nitrate is used. As silver nitrate was used in this investigation that only very closely approached absolute purity,the inclusions must be considered greater than this. Taking the inclusions as 10 parts per 100,000,the limits of error would come to plus 5 to plus 15 parts per 100,000, which is very small when compared with the difference obtained between the two kinds of deposits.

The action of the liquid ammonia coulometer when the current was turned on may be described as follows. The heat generated by the current in the electrolyte caused it to boil very gently. The bubbles of gaseous ammonia did not

come from the body of the liquid,but came off the cathode and the porous anode cell. Nearly always large bubbles came off from just one spot on the cathode. This fact shows that the gas formed is not one of electrolytic deposition but merely the vaporization of the ammonia due to the heating effect of the current. Without any doubt,this bubbling phenomenon is beneficial rather than harmful,since it serves to keep the electrolyte stirred up,and does not permit the concentration of silver ions to decrease to a dangerous point in the immediate vicinity of the cathode.

Because of the smoothness of the deposit,it would be impossible to tell by observation that any silver was being formed were it not for the peculiar color changes that take place. Almost at the same instant that the current is turned on,the cathode takes on a light yellow color. In most cases this later changes to a black,but sometimes at the finish of a run the cathode is still a very light yellow or pink color. A very decided copper color is sometimes met with. The conditions which determine the color of the deposit seem to be very obscure,and as yet it has not been possible to formulate them. The most likely explanation of the color phenomenon is that the silver is deposited in a colloidal state,and the yellow,black,pink and intermediate colors

indicate different sized particles.

When the investigation was started,the cathode was simply removed and washed with water and alcohol,after the ordinary manner of treating deposits. The color of the deposit was not considered very seriously,since silver in the colloidal state would weigh the same as any other silver. The deposit was found to be considerably heavier than that on the standard coulometer,however,and the only theory that could be advanced for this discrepency was the inclusion of large amounts of impurities.

It was for the purpose of trying to remove any silver compounds present in the deposit that a thorough soaking in aqueous ammonia was tried. The ammonia would dissolve out any silver compound due to the formation of the complex silver ammonia ion,but would leave the metallic silver unchanged. This was tried,and the cathode was then heated for one hour in an open dish over a Bunsen burner. The results of this experiment were very encouraging. On heating,the cathode became a very beautiful white,and the quantitative results showed that it weighed about 25 parts in 100,000 less than the standard deposit. This was a little greater than the limit of error of the standard coulometer,but it was thought that more accurate determin-

ations would show that the deposit from liquid ammonia was purer than that from water. The experiment was repeated many times under exactly the same conditions as those above and special pains were taken as to the accuracy of manipulation. In every case,however,the results showed that the liquid ammonia silver deposit was quite noticeably heavier than the standard. Longer soaking in the ammonia water and heating right up to the melting point only lessened the difference a little,the smallest difference observed being three tenths of one per cent.

The following table gives a very brief summary of the results of those runs where quantitative determinations were made.

Run No.	Washing of Cathode	Heating of Cathode	% Heavier than Stan.	Remarks
1	Same as standard coulometer	Same as standard coulometer	.6	Deposit made on platinum crucible. Copper colored
5	Rinsed with water and alcohol	Dried over open flame	2.6	Current .020 amperes. Deposit black, changes copper
6	Rinsed with water and alcohol	Porcelain dish over Bunsen burner	1.6	Current .020 amp.Deposit black,brighter on heating
6	Rinsed with water and alcohol	Assay furnace nearly to melting point	.3	Same as above Bright silver white,blistered somewhat
7	Soaked in NH_3 water, rinsed with alcohol	Porcelain dish over Bunsen burner	-.025	Silver white
8	Soaked in NH_3 water, rinsed with alcohol	Porcelain dish over Bunsen burner	.6	Current,.070 amp.
10	Soaked in NH_3 water, rinsed with alcohol	Porcelain dish over Bunsen burner	.9	Current .100 amp.Dep.white but speckled
12	Soaked in NH_3 water, rinsed with alcohol	Porcelain dish over Bunsen burner	1.4	Current .100 amp. Deposit rather dark
13	Soaked in NH_3 water, rinsed with alcohol	Blast lamp furnace	.7	Current .100 amp. Cathode pinkish yellow before heating
15	Soaked in NH_3 water several hours	Blast lamp furnace	.5	Current .100 amp. Cathode very bright after heating

From the summary of results given in the above table, only one conclusion is possible. The inclusions in silver deposited from liquid ammonia are much greater than in the ordinary coulometer. The one contradictory run,No.7,cannot be considered,since the result obtained there was never repeated. Sometimes when the cathode was rinsed too soon after removal from the bath,the sudden change of temperature caused fine particles of silver to fly off. Too sudden heating also made the same thing happen. The discordant result of this run is probably due to an accident similar to these two mentioned.

In Run No.1,the total deposit was very small,so that the results perhaps do not give as accurate an indication as a heavier deposit would. It is significent,however,that the percentage heavier than the standard in this run was only .6%,thus comparing well with runs where the washing and heating were much more thorough. The logical conclusion is that the inclusions near the surface may be removed easier than those deeper down.

A comparison of No.5 and the second No.6 illustrate better than any others the effect of heating the cathode. In No.5,practically no heating at all was done-only enough to evaporate off the alcohol. No.6 was heated the second

time in a white hot assay furnace nearly to the melting point. The decrease from 2.6% inclusion to .3% was the result.

The treatment with ammonia water did not have the marked effect the heating had,but was beneficial,nevertheless. Nearly the same conditions of heating prevailed in the first part of Run No.6,and in Nos.8,10 and 12. The percentage of impurity was reduced from 1.6 in No.6 to .6,.9 and 1.4 in Nos.8,10 and 12,respectively. In Runs 13 and 15,the conditions of heating were practically identical. In No.15,the cathode was soaked for an extra long time in the ammonia water. The decrease from .7% to .5% was the result.

Further than the heating and washing of the cathode, no conditions could be found that changed the amount of inclusion. Of course,as mentioned before,the light deposit (.036 g.) in No.1 was suspected of influencing the fact that such a comparitively low amount of included matter was present. The other deposits varied from .5 g. to over 1 g.,but no relation was observed between the weight of deposit and the percentage of inclusion. Current density did not seem to have any effect on the purity of the deposit,since just as good results were obtained with .004 amp. per sq.cm. as with .001 amp. per sq.cm.

CONCLUSION

The silver deposit is very coherent and from this fact possesses an advantage over the loose crystalline deposit of the ordinary coulometer. This advantage refers,of course, merely to the mechanical loss in washing,and is lost if the temperature of the cathode is changed very suddenly, with the consequent loss of silver particles thrown off by the sudden contraction or expansion. It is this very coherency,however,that causes the large amount of included matter. As the silver deposits in the colloidal form, many fine interstices are left between the particles, which provides a place for the silver nitrate nitrate solution to lodge. As this is immediately covered over with a tight deposit of more colloidal silver,the inclusion is protected from the effect of washing,either with water or aqueous ammonia,and all that the heating would do would be to decompose the silver nitrate and other impurities,thereby getting rid of part of the inclusions but never all of them. As proof of the fact that some of the inclusion is given off on heating,it has been observed that sudden and violent heating causes blisters to form on the skin of the deposited silver. Most of the inclusion before heating consists of silver nitrate,as the main part of the liquid ammonia would vaporize and work out

through the pores of the silver soon after removal from the bath. On heating this silver nitrate would decompose to the oxide or to free silver.

A rather interesting experiment was tried,-making a run with a strong aqueous ammonia solution of silver nitrate. The deposit on the cathode was not smooth,but had the broken appearance of the ordinary water deposit. Each particle,however,instead of being angular and crystalline, was rounded and smooth in appearance. Although no quantitative determination was made,it would probably show the presence of large quantities of impurities.

The fact that stands out in all silver coulometry is that the more coherent the deposit is,the more likelihood there is of being included matter. Ordinary silver nitrate containing a minute amount of silver acetate gives deposits heavier than those from the purest silver nitrate.* Not only are these deposits heavier,but they are finer and more coherent,which fact alone may explain the increased inclusions.

As to the value of the liquid ammonia silver coulometer, it must be limited to determinations not requiring an accuracy greater than one half per cent. A correction might be

*Trans.Amer.Electrochem.Soc.,Vol.22.,p.363.

made for included impurity,but as the amount of this varies so,no great accuracy could be obtained even then. Two factors seem to be highly important in rendering the inclusions as small as possible;these are(1)a thorough soaking in aqueous ammonia,and(2)heating nearly to the melting point of silver. A reasonably high current density does no harm because of the stirring effect of the ebullition of liquid ammonia. With a correction for inclusions,the liquid ammonia silver coulometer should be fully as accurate as an ordinary copper coulometer.

As compared to the standard silver coulometer,the latter stands far superior in accuracy. The advantages possessed by silver deposited from liquid ammonia lie in the fact that the deposit is firm and coherent with little chance for mechanical loss and also in the fact that there is no tendency whatever to sprouting or growing out in fine threads over to the anode.

It is suggested that a promising field for further research is to find some method that will prevent the silver depositing in colloidal form. The writer believes that if this were accomplished,the deposit would be much improved from the viewpoint of included matter.

In conclusion,the writer wishes to express his sincerest thanks to Dr.H.P.Cady for the assistance and advice he has offered at all times. His most valuable suggestions are the basis for most of the investigation. The writer also wishes to extend his appreciation to Dr.P.V.Faragher for his final reading of the original paper,and to Prof.W.A.Whitaker,Jr. for his practical advice and suggestions on the treatment of silver.